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(21) International Application Number: PCT/US93/12036 (22) International Filing Date: 10 December 1993 (10.12.93) (30) Priority Data: 997,374 28 December 1992 (28.12.92) US (71) Applicant: ADVANCED PRODUCTS, INC. [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US). (72) Inventors: BUCKLEY, Michael, Sean; 23125 Rio Lobos Road, Diamond Bar, CA 91765 (US). BOWNS, Richard, Earl; 16326 Halliburton, Hacienda Heights, CA 91745 (US). (74) Agents: SIMONS, William, A. et al.; Wiggin & Dana, One Century Tower, New Haven, CT 06508-1832 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FL, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: WATER-BASED POLYMER THICK FILM CONDUCTIVE INK		
(57) Abstract <p>The present invention relates to an aqueous conductive polymer thick film-forming composition comprising a water-soluble thermoplastic polymer, a polymer dispersion in water, a glycol drying-retarder agent, an electrically conductive amount of conductive metal and/or carbon particles and water. The composition in the production of a highly printable conductive thick film ink.</p>		

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WATER-BASED POLYMER THICK FILM CONDUCTIVE INK

This invention relates generally to aqueous polymer thick film conductive compositions containing conductive metal, carbon or graphite particles. The compositions are particularly useful
5 for screening into electrical circuits and for formulation into human contact electrodes.

In the past, water-based conductive polymer thick film formulations have typically exhibited poor rheology, poor adhesion and poor flexibility
10 when printed and cured on polyester or polycarbonate films. They also have not offered the relatively low electrical resistance that is achievable with solvent based formulas.

In view of the above, new aqueous compositions which provide a solution to the above problems while containing a reduced amount of organic solvents, relative to conventional solvent-based thick film formulations, would be highly desired by the polymer thick film manufacturing community. The present
20 invention provides one solution to this problem. This invention relates to the use of water soluble thermoplastic polymers in a water-based polymer thick film-forming compositions to impart smooth, easily spreadable coating qualities to the
25 formulation.

In one aspect, the present invention relates to an aqueous conductive polymer thick film-forming composition comprising (preferably consisting essentially of):

- 30 (a) a water soluble thermoplastic polymer in an amount of between about 0.25% and about 20% by weight;
- (b) a polymer dispersion in water in an amount of between about 10% and about 70% by weight;
- 35 (c) a glycol drying-retarder agent(s) in an amount of between about 2% and about 20% by weight;

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5 (d) an electrically conductive amount of
conductive particles selected from the group
consisting of conductive metal (preferably
silver flake), carbon, and graphite particles,
and combinations thereof, with the proviso that
the amount of said metal particles does not
exceed 90 % by weight and the amount of said
carbon or graphite particles does not exceed
40% by weight; and

10 (e) water in a solvent effective amount, each
of said amounts being based upon the total
weight of said composition.

This and other aspects will become apparent
upon reading the following detailed description of
15 the invention.

In accordance with the present invention, an
aqueous conductive polymer thick film-forming film
composition is provided which provides excellent
film properties, such as resistivity and
20 printability, during use. The compositions provide
a distinct advantage from an environmental
standpoint since they are water-based. These
compositions are useful as highly printable
conductive inks utilizing screen printing or other
25 conventional printing method. These inks are of
such highly printable quality that lines and spaces
15 mils wide can be clearly printed. This highly
printable quality is important in order to
effectively print the intricate circuitry patterns
30 often demanded by the electronics industry in high
performance applications such as, for example, in
the preparation of touch pad circuitry.

Examples of suitable thermoplastic water
soluble polymers useful in the present invention
35 include polyethyloxazoline, polyvinyl pyrrolidone,

polyvinyl alcohol, polyacrylamide, polyglycols and polyacrylic acid.

Examples of suitable polymer dispersions in water include polyurethane, acrylic, polyester and vinyl resin polymers.

The purpose of the glycol drying retarding agent(s) employed in the present invention is to slow down the drying process so as to permit manipulation of the polymer thick film, such as by silk screening, before it has a chance to dry. Examples of suitable glycol type drying retarding agents include: diethylene glycol ethyl ether acetate; diethylene glycol butyl ether acetate; ethylene glycol butyl ether acetate; diethylene glycol monoethyl ether; ethylene glycol monoethyl ether; dipropylene glycol methyl ether; tripropylene glycol methyl ether; dibutyl phthalate; diocyl phthalate; diocyl phthalate; tributyl phosphate; 1,3 butylene glycol; propylene glycol and ethylene glycol. These agents may be used singularly or in combination with each other.

Any conductive metal particle may be used in the composition of this invention such as copper, gold, nickel, silver alloys, silver plated metals and silver. Silver is the preferred conductive particle for most uses. Alternatively, carbon black or graphite may also be used, alone or in combination with metal particles.

The average particle size of the metal or carbon or graphite particle can vary over a wide range but, is preferably in the range of from about 1 micron to about 50 microns, more preferably from about 2 microns to about 20 microns. If the average particle size of the metal particles is less than about 1 micron, the electrical properties may be adversely affected. In other words, if the metal

particles are too fine, the resistivity of the composition may be too high. If the average particle size of the metal particles is above about 50 microns, then the composition will be too
5 difficult to apply to the substrate. For example, the composition will tend to clog up during a silk screening process or the like.

Other minor conventional components may be added to the conductive composition. These include
10 viscosity modifying agents and defoaming surfactants. The viscosity of the final conductive composition of this invention for screen printing is preferable from about 8,000 to about 25,000 centipoises at 30°C (Brookfield RVT Spindle #6 at 20
15 rpm) in order to be screen printable.

The compositions of this invention may be applied to substrates by a variety of techniques, such as silk screening, spraying or brushing. Once the conductive polymer thick film has been applied
20 to the substrates it is cured at between about 93°C and 135°C for a time sufficient to complete curing with good adhesion.

The conductive compositions of the present invention may be applied to conventional rigid or
25 flexible substrates. Whether the substrate is flexible or rigid in nature, the substrate may or may not have to be pre-treated or pre-coated with any other substance before applying the present composition.

30 EXAMPLE 1

Preparation of an Aqueous Polymer Thick Film-forming Composition Using Silver Flake

A 40% solution of Peox in water was made using a cowles mixer. This solution was then vigorously
35 hand mixed with the rest of the mixture's components

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as identified in the table hereinbelow. The resulting mixture was then passed through a three roll mill to provide the desired film-forming composition.

5	Composition	Weight
	<u>Component</u>	<u>in Parts Per 100/Wt</u>
	Peox (Polyethyloxyazoline) (1)	2.80
	AW875 (2)	20.38
	Silver Flake (3)	55.25
10	H ₂ O	16.22
	Diethylene Glycol Mono Ethyl Ether	5.22
	BYK020 (4)	0.13

The properties of the film-forming composition were as follows:

15	Electrical resistivity	19 milliohms/sq. @ 1.0 mil
	Printability	Very good
	Adhesion	<2% in resistance
	Print Quality	Good

EXAMPLE 2

20 Preparation of Another Aqueous Polymer Thick Film- Forming Composition Using Silver Flake

25 A 55% solution by weight of PVP K-30 in H₂O was made using a cowles mixer. This solution was then agitated with the rest of the mixture's components as identified in the table hereinbelow. The resulting mixture was then passed twice through a three roll mill to provide the desired film-forming composition.

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	<u>Component</u>	<u>Parts per 100</u>
	PVP (5)	1.09
	AW875	28.15
	Ethylene Glycol	7.52
5	H ₂ O	1.96
	Witco 748 (6)	.6
	Triton CF-10	.6
	Silver Flake	60.08

10 The properties of the film-forming composition were as follows:

	Viscosity	10,150 CPS
	(Brookfield #6 spindle @ 20rpm, 25°C.)	
	Resistivity	17 milliohms/sq. @ 1.0 mil
	Adhesion	<2 in resistance
15	Flexibility	
	1 crease	+10%
	3 crease	<+150%

EXAMPLE 3

20 Preparation of an Aqueous Polymer Thick Film-forming
Composition Using Carbon Particles

25 A 55% solution of PVP K-30 in H₂O was prepared using a cowles mixer. This solution was then agitated with the rest of the mixture's components as identified in the table hereinbelow. The resulting mixture was then passed twice through a three roll mill to provide the desired film-forming composition.

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	<u>Component</u>	<u>Parts per 100</u>
	Carbon (XC-72) (8)	6.26
	AW875	60.88
	Triton CF-10	2.60
5	PVP K-30	2.46
	Ethylene Glycol	16.31
	H ₂ O	10.34
	Witco 748	1.15

10 The properties of the film-forming composition were
as follows:

Resistivity	1700 ohms/sq. @ 1.0 mil
Printability	Good

15 The following is a list of sources for the
various trademarks/tradenames used in the above
three examples.

- 1) "Peox" is a water and solvent soluble polymer polyethyloxazoline previously available from Union Carbide, 39 Old Ridgebury Road, Danbury, CT 06817-0001.
- 20 2) "AW875" is a vinyl resin dispersed in water, available from Union Carbide, 39 Old Ridgebury Road, Danbury, CT 06817-0001.
- 3) "Silver flake" is available from Chemet Corporation, 52 Gardner Street, Attleboro, MA 02703.
- 25 4) "BYK020" is a defoamer available from BYK Chemie USA, 524 South Cherry Street, Wallingford, CT 06492.
- 5) "PVP K-30" is a polyvinyl pyrrolidone polymer, soluble in H₂O, available from GAF Chemicals Corporation, 1361 Alps Road, Wayne, NJ 07470.
- 30

- 6) Witco "Bubble Breaker 748" is a defoamer available from Witco Organics Division, 3230 Brookfield Street, Houston, TX 77045.
- 7) "Triton CF-10" is a surfactant available from Union Carbide, 39 Old Ridgebury Road, Danbury, CT 06817-0001.
- 8) "XC-72" is a carbon powder available from Cabot Corporation, 125 High Street, Boston, MA 02110.

10 In addition, as used in the above examples, the "adhesion" test refers to the percentage change in resistance after applying Scotch tape to a test pattern of the ink and then removing the tape and remeasuring the resistivity. Similarly, the
15 "flexibility" test measures the percentage change after creasing the test pattern which was silk screened for each example.

While the invention has been described above with reference to specific embodiments thereof, it
20 is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the
25 spirit and broad scope of the appended claims. All parts and percentages are by weight unless otherwise explicitly stated.

WHAT IS CLAIMED IS:

1. An aqueous conductive polymer thick film-forming and printable composition characterized by:

- 5 (a) about 0.25% to about 20% by weight of water-soluble thermoplastic polymer selected from the group consisting of polyethyloxazoline, polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide, polyglycol, and polyacrylic acid;
- 10 (b) about 10 to 70% by weight of a polymer dispersion in water, said dispersed polymer selected from the group consisting of polyurethane resin polymer, acrylic resin polymer, polyester resin polymer, and vinyl resin polymer;
- 15 (c) about 2% to about 20% by weight of at least one glycol drying-retarder agent;
- 20 (d) an effective electrically conducting amount of less than 90% by weight of conductive particles selected from the group consisting of conductive metal particles, carbon black particles, graphite particles, and combinations thereof; with the proviso that the amount of
- 25 said carbon black particles, graphite particles, or combinations thereof do not exceed 40% by weight; and
- 30 (e) an effective solvating amount of water to dissolve water-soluble thermoplastic polymer (a);
- each of said amounts being based upon the total weight of said composition.

2. The composition of claim 1 characterized in that said water-soluble thermoplastic polymers is polyethyloxazoline.

35

3. The composition of claim 1 characterized in that said water-soluble thermoplastic polymer is polyvinyl pyrrolidone.

5 4. The composition of claim 1 characterized in that said dispersed polymer is vinyl resin polymer.

5. The composition of claim 1 characterized in that said glycol drying-retarding agent is ethylene glycol.

10 6. The composition of claim 1 characterized in that said conductive particles are silver flake.

7. The composition of claim 1 characterized in that additionally comprising viscosity modifying agents and defoaming surfactants.

15 8. The composition of claim 1 characterized in that said conductive particles are from about 1 micron to about 50 microns.

20 9. A process for using the composition of claim 1 characterized by applying said composition to a substrate and drying said composition at an elevated temperature to provide a polymer thick film conductive ink on said substrate.

10. The process of claim 9 characterized in that said elevated temperature is between 70°F and 300°F.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US93/12036**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :HO1B 1/00, 1/20, 1/22, 1/24

US CL :252/502, 511, 512, 574, 518; 106/1.18, 1.25; 524/501, 503

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/502, 511, 512, 574, 518; 106/1.18, 1.25; 524/501, 503

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: SEE ATTACHED

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,510,275 (HIKURA ET AL.) 09 APRIL 1985 SEE ABSTRACT; COL 6 LINES 54-55; COL 9 LINES 1-7.	1-10
A	US, A, 5,137,542 (BUCHANAN ET AL.) 11 AUGUST 1992 SEE ABSTRACT; COL 7 LINES 27-36.	1-10
A	US, A, 4,853,285 (SOBATA ET AL.) 1 AUGUST 1989 SEE ABSTRACT; COL 4 LINES 4-14; COL 11 LINES 12-20.	1-10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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